Nanocatalysis in Solution

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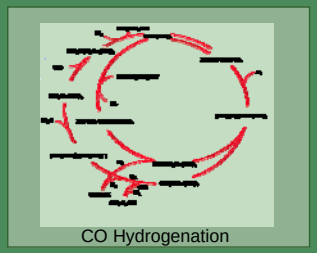
Problem

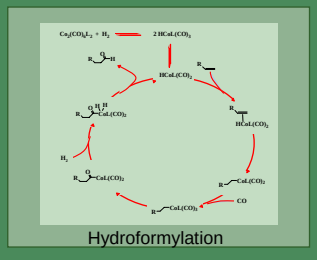
The determination of reaction pathways for heterogeneous systems is often complicated since their reaction kinetics are frequently dominated by physical sorption/desorption processes rather than the salient bond-making/breaking steps in homogeneous systems. Consequently, solution-phase spectroscopic methods (e.g., infrared and UV/Vis spectroscopies, high resolution NMR) have little impact.

Solution

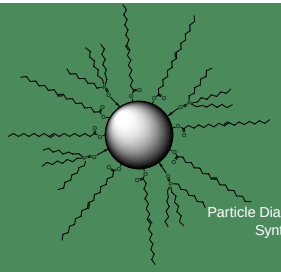
Using soluble, ligand-stabilized nanoparticles, it is possible to utilize solution phase spectroscopic methods as well as surface techniques (e.g., scanning and transmission electron microscopy, X-ray absorption fine structure, small angle X-ray scattering) which should allow more in-depth mechanistic studies and facilitate the identification of reaction intermediates. We have used solution techniques previously to elucidate the catalytic cycle for CO hydrogenation and have contributed insights to the commonly accepted olefin hydroformylation mechanism (below).



CO Hydrogenation



Hydroformylation

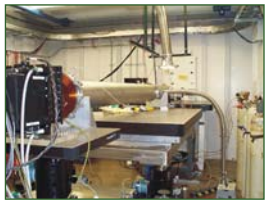


Ferromagnetic cobalt nanoparticles†

Particle Diameter:	9.5 nm
Synthesis:	Decomposition of $Co_2(CO)_8$ with nucleation at 180ºC; growth at 130ºC for 1 hour
Capping Ligands:	Oleic acid (0.4 equiv.) and trioctylphosphine oxide (0.16 equiv.)
Number of Cobalt Atoms:	~ 40,000
% Cobalt Atoms at Surface:	~ 15 %

High Pressure NMR

(nuclear magnetic resonance)

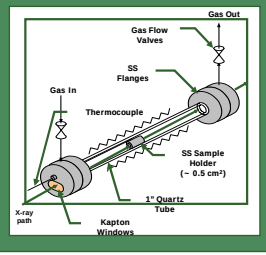


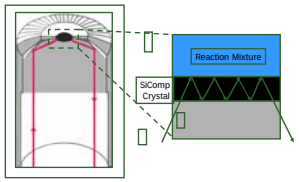
SAXS

(small angle X-ray scattering)

XAF

(X-ray absorption fine structure)





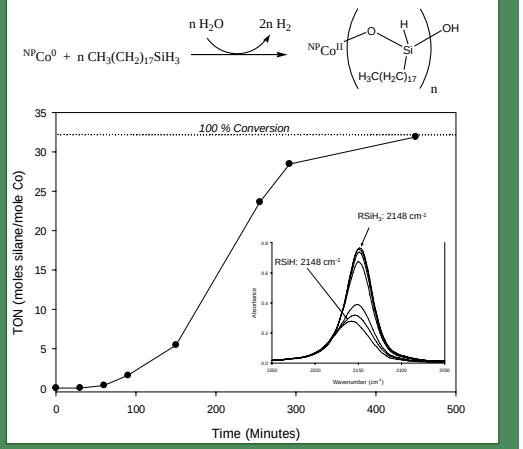
High Pressure ATR/IR

(attenuated total reflectance infrared)

Preliminary Results

Ferromagnetic cobalt nanoparticles (shown at left) catalyze the hydrolytic polymerization of octadecylsilane to form polysiloxane chains that remain chemically bound to the nanoparticle. When precipitated, these polymer chains are susceptible to magnetic fields. The particles appear to have good thermal stability at the temperatures currently used (up to 100ºC) without precipitation.

Activity of Cobalt Nanoparticles for Hydrolytic Octadecylsilane Polymerization at 60° C in 1,2-Dichlorobenzene



Conclusions and Future Work

Hydrolytic polymerization of silanes likely involves oxidative addition of Si-H bonds to cobalt. Consequently, current studies investigate these nanoparticles as olefin hydrosilation catalysts using silanes with only one Si-H bond (e.g., triethylsilane). Utilization of high pressure *in situ* infrared spectroscopy (shown at left) will help monitor these reactions in real-time. Magnetic susceptibility studies *via* NMR spectroscopy will help track changes to the nanoparticle catalyst under the reaction conditions.

† Samia, A.C.S.; Hyzer, K.; Schlueter, J.A.; Qin, C.; Jiang, J.S.; Bader, S.D.; Lin, X. *J. Am. Chem. Soc.* **2005**, *127*, 4126-4127

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